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6. AUTHOR(S)
Robert W. Field and Robert J. Silbey

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139-4307

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13. ABSTRACT (Maximum 200 words)

Through Stimulated Emission Pumping (SEP) studies of highly excited vibrational levels of the electronic ground state of HCP, the spectroscopic signatures of bond-breaking isomerization (HCP↔HPC) were detected and interpreted for the first time. Two novel spectroscopic schemes, UV excited-IR detected fluorescence excitation spectroscopy and UV excited-Auger detected Laser Excited Metastable (LEM) spectroscopy, prove the existence of a Gateway Mediated Inter-System Crossing (GMISC) mechanism in acetylene. In GMISC, one special vibronic state couples the single bright state to a dense manifold of dark states. The complementarity of LEM and Laser Induced Fluorescence (LIF) spectroscopies was found to be ideally suited for study of ISC, because LEM is blind to short-lived radiating states and LIF is blind to metastable states. A pattern recognition technique, Extended Cross Correlation (XCC), which is capable of picking out multiple patterns that are repeated in multiple spectra without any prior knowledge of the forms of the patterns, was applied with extraordinary success to several types of spectra. Among these was a data set consisting of electron beam excited infrared spectra of CO, recorded by Dr. Stephen Lipson and colleagues at the Air Force Phillips Laboratory. All of the severely overlapped features were "unzipped," assigned, and independently represented by time dependent populations.

The central theme in each of these projects is the development of experimental methods, theoretical models, and pattern-recognition schemes capable of extracting previously inaccessible information from spectra of highly excited molecules.

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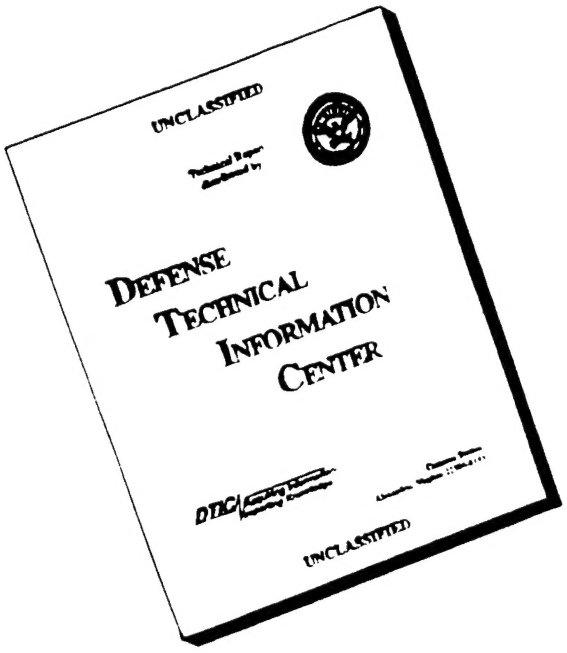

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Final Report

to

Air Force Office of Scientific Research

Large Amplitude Motions in Polyatomic Molecule Spectra: Intramolecular Vibrational Redistribution and Isomerization
F49620-94-1-0068

Presented by:

Robert W. Field
Professor of Chemistry
and
Robert J. Silbey
Professor of Chemistry

Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, Massachusetts 02139-4307

Period: 1 December 1993 - 30 November 1996

TABLE OF CONTENTS

A. Final Report 1 December 1993 - 30 November 1996

1. LIST of Personnel

a. Graduate Students

Jonathan	Bloch	(Ph.D. 5/96)[1]
Jason	Clevenger[1]	
Kevin	Cunningham	
Ilia	Dubinsky[3]	
Christopher M.	Gittins	(Ph.D. 2/95)[1]
Matthew	Jacobson[4]	
Neme	Nnolim	(M.S. 9/95)
Jonathan P.	O'Brien[2]	
Bhavani	Rajaram	(Ph.D. 1/95)
Leah	Ruslen[2]	
Gunther	Schmid[6]	
Michelle	Silva	
Stephani Ann B.	Solina	(Ph.D. 5/96)[2,5]
Jianghong	Wang	(M.S. 5/94)

1. Primary support NSF
2. Primary support DOE
3. Primary support J. Steinfeld NASA
4. DOD Predoctoral Fellow
5. NSF Predoctoral Fellow
6. Primary Support R. Silbey NSF

b. Postdocs and Visitors

Dr. Stephen	Coy[1]	
Dr. Stephen	Drucker	
Dr. Brian	Gilbert	(now at Coastal Carolina Univ.)[4]
Dr. Haruki	Ishikawa	(now at Tohoku University)[2]
Dr. Bing	Ji	(now at Air Products Corp.)[5]
Prof. Marsha	Lester	(U. of Pennsylvania)[3]
Dr. David	Moss	(Boston University)[6]
Prof. William	Polik	(Hope College)[3]
Prof. Richard	Redington	(Texas Tech University)
Prof. Curt	Wittig	(U. of Southern California)[3]

1. Consultant
2. JSPS Fellow
3. Sabbatical Visitor
4. Primary support RWF-JIS NASA
5. Primary Support NSF
6. Primary support ACS-PRF

c. Undergraduate Students

Heather Drake
Ana Isasi
Jonathan Katz
Maya Kaushal
Donald Lucas
Paresh Patel
Jennifer Sokol

d. Collaborators

Dr. Michael Davis	Argonne National Lab	pattern recognition
Prof. Edward E. Eyler	U. Connecticut	Pulsed FM
Prof. Robert Gordon	U. Illinois, Chicago	Deperturbation HCl
Prof. Fritz Grein	U. New Brunswick	HCP *ab initio*
Dr. John Hall	JILA	$^{13}C_2H_2$ Isomerization by NICEOHMS
Prof. Joshua Halpern	Howard U.	Cyanogen
Prof. Michel Herman	Bruxelles	HCCH
Prof. Michael Kellman	U. Oregon	pattern recognition
Prof. Kevin Lehmann	Princeton	Intracavity MRS Unzipping Isotopic NH_3
Dr. Stephen Lipson	AF Phillips Lab	pattern recognition
Dr. Edmond Murad	AF Phillips Lab	ionization energies
Dr. Eric Rohlfing	DOE, Combustion Research Facility	Unzipping Vinoxy
Dr. Reinhard Schinke	MPI Gottingen	HCP
Dr. Trevor Sears	Brookhaven National Lab	FM, HCBr
Prof. Alec Wodtke	UC Santa Barbara	triplets
Prof. Robert Wyatt	U. Texas	patterns in *ab initio* spectra

2. REPORT ON RESEARCH PROJECTS

a. HCP Isomerization

This is one of three most important results from this grant.

HCP is the first example in which a bond-breaking isomerization process is sampled by an eigenstate-resolved spectrum. The spectroscopic signature of isomerization, a change in the $\omega_1 : \omega_2 : \ldots \omega_{3N-6}$ vibrational resonance structure as manifest in sudden modifications of spectroscopic patterns, is observed in the Stimulated Emission Pumping (SEP) spectrum of the HCP $\tilde{X}\,^1\Sigma^+$ electronic state (recorded via the $\tilde{A}\,^1A''$ and $\tilde{C}\,^1A'$ intermediate states). The SEP spectra of the HCP $\leftrightarrow$ HPC isomerization process provide examples of several general methods for recognition, analysis, and interpretation of unimolecular isomerization. These include: (i) a sudden onset of (a new class of) spectroscopic perturbations; (ii) a sudden change (departure from normal v,J-scaling) of vibration-rotation fine structure constants; and (iii) the appearance of new classes of vibrational states with anomalously large or small rotational constants. It is essential to be able to follow a long vibrational progression (not necessarily in the normal mode that couples most strongly to the minimum energy isomerization path) continuously up to vibrational energies above the *ab initio* predicted isomerization barrier (or saddle point). It is also essential to have a larger scale spectroscopic pattern, such as the cluster of mutually interacting states that belong to the same value of polyad quantum number(s). In HCP, the 2:1 resonance between the CP stretch (mode 3) and the bend (mode 2), $\omega_3 \approx 2\omega_2$, provided the polyad (polyad quantum number $P = v_2 + 2v_3$) pattern that enabled us to make definitive vibrational assignments of the complicated appearing spectrum at $E_{VIB} \leq 25{,}000\ cm^{-1}$.

In a continuing collaboration with Dr. Reinhard Schinke's group at the Max Planck Institüt für Stromungsforschung in Gottingen, we first were able to show that all of the dramatic changes observed in the SEP spectrum of HCP were due to the decrease in the H–X (X is the center of mass of CP) stretch from $\sim 5\omega_{bend}$ to slightly less than $3\omega_{bend}$ and then back to slightly more than $3\omega_{bend}$ at linear HPC. This change in resonance structure accounts for the sudden turning on near $v_{bend} = 32$ of anharmonic ($4\omega_{bend} \approx \omega_{HX}$) and Coriolis ($3\omega_{bend} \approx \omega_{HX}$) perturbations, the rapid change of all fine structure parameters (defined by second order perturbation theory), and the appearance of an anomalously large-B polyad of $\ell = 0$ substates. Schinke also predicted a class of delocalized states (the "saddle node" SN states), which were subsequently observed by Ishikawa et al in his SEP experiments at Tohoku University. These SN states are the first experimentally observed example of over-the-barrier delocalized states.

The experimental study of HCP at MIT is terminated, but is continuing in Professor Ishikawa's group at Tohoku University. Our collaboration with Ishikawa (experiment) and Schinke (Theory) is continuing. We expect to summarize the new experimental measurements (on the SN states and on the postulated small-B $\ell = 1$ states that are responsible, via Coriolis perturbations, for the large-B $\ell = 0$ states) in several publications, culminating in a review article in Ann. Revs. Phys. Chem.

b. Triplet States of Acetylene

This is one of the three most important results from this grant and is the central focus of the continuing grant (F49620-97-1-0040).

We have observed intersystem crossing (ISC) in acetylene by qualitatively new types of experimental schemes: IR detected ($T_{2,3} \rightarrow T_1$)-UV excited ($S_1 \leftarrow S_0$) fluorescence excitation and Auger-detected (T_3), UV-excited "Laser Excited Metastable" (LEM) spectroscopy. A report of the former experiment will appear as a Communication in JCP and a report of the latter experiment has recently been submitted as a Communication to JCP. The unifying theme of both experiments is that it is now possible to characterize the ISC mechanism more completely. Instead of a simple model of one "bright state" coupling to a dense manifold of "dark states," we have proposed a "gateway mediated" ISC mechanism whereby one bright state couples to a single gateway state which in turn couples to a dense manifold of dark states. In the case of S_1 acetylene, the gateway is a single low vibrational level of the T_3 triplet surface (the upper sheet of the Renner-Teller split electronic state that correlates with $\pi_u^3\pi_g^* \, ^3\Delta_u$ in linear geometry).

The LEM experiments were carried out in Alec Wodtke's laboratory at UCSB. A supersonic beam of C_2H_2 in H_2, He, or Ne was excited via various $\tilde{A}$ - $\tilde{X}$ bands, including the $V_0^4K_0^1$ band which terminates in an upper state 200 cm^{-1} above the $C_2H_2 \rightarrow H + CCH(\tilde{X})$ dissociation limit. Metastable species are detected by ejection of an Auger electron from a Au electrode (work function 5.1eV). The high work function of the Au electrode requires T_3 or S_1 character for Auger detection, and the ~200μs flight time from excitation to detection restricts the fractional S_1 character to <1%. Therefore LIF and LEM schemes are complementary; one is blind to triplets and the other is blind to singlets. The LEM scheme is able to distinguish intact C_2H_2 metastables from metastable photofragments (C_2H, C_2, and CH). The observation of intact metastable 200 cm^{-1} above the dissociation limit has startling photochemical consequences. The LEM spectrum exhibits two interference features, which are the universal signature of the gateway mediated mechanism, and in the present case serve to locate the J-value of the level crossing between the bright (S_1 $3v_3$) and gateway (T_3) states.

We expect to record a series of higher resolution (~ 0.01 cm^{-1}) LEM spectra at UCSB in order to better characterize the gateway state. We have nearly completed construction of a complementary electron bombardment supersonic jet source of C_2H_2 metastables at MIT.

c. Pattern Recognition

Modern spectroscopic techniques are capable of generating enormous quantities of high quality (spectral and temporal resolution, quantitative intensities over large dynamic range) spectra. We have developed a special kind of pattern recognition scheme which is capable of picking out patterns that appear in multiple spectra without making any assumptions about the form of the pattern. This scheme, which we call Extended Cross Correlation (XCC) and Extended Auto-Correlation (XAC), has been applied to several classes of spectra: (i) dispersed fluorescence (DF) spectra of C_2H_2 $\tilde{A} \rightarrow \tilde{X}$; (ii) IR spectra of CO pulse-excited by a kV electron beam; and (iii) FTIR absorption spectra of $NH_3/NDH_2/ND_2H/ND_3$ (recorded at Kitt Peak Solar Observatory) at a series of H : D isotope ratios.

The DF spectra of C_2H_2 are the primary subject of a DOE grant. The SCC method (developed jointly by Steve Coy and Matt Jacobson, supported respectively by AFOSR and a DOD fellowship) has enabled us to "unzip" the spectrum into overlapping polyads, from which we have been able to deduce the nature and rates of the dominant energy flow pathways, which are collectively known as Intramolecular Vibrational Redistribution (IVR). Guided by our AFOSR supported study of the signature of isomerization in HCP, we are about to attempt to unzip the DF spectra of HCCH in the energy region of the acetylene↔vinylidene isomerization barrier. We expect to detect the onset of isomerization via the change in $\omega_1 : \omega_2 : \ldots \omega_{3N-6}$ resonance structure, as revealed by a departure of the polyad structure from vibrational scaling predictions.

A collaboration between Matt Jacobson and Dr. Stephen Lipson at the Air Force Phillips Laboratory is the most important "transition" of this AFOSR project. The following abstract has been submitted for clearance at Phillips Laboratory, and will be the basis for talks by Dr. Lipson (at the Spring meeting of the American Geophysical Union) and Mr. Jacobson (at the 52nd International Symposium on Molecular Spectroscopy, Ohio State University):

InfraredSpectral Data Analysis and Remote Sensing Using Pattern Recognition Algorityms; *S.J. Lipson, R.B. Lockwood, D.L. Vititoe, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, and R.W. Field.*

In remote sensing of atmospheric spectra, the complexity of analyzing data may be compounded by extreme departures from thermodynamic equilibrium, and by spectral overlaps, temporal variation, and lack of knowledge of line-of-sight effects. We have developed algorithms for the analysis of infrared spectral data taken under these conditions, and applied them to the study of highly vibrationally and rotationally excited carbon monoxide observed in atmospheric simulation experiments. The data were taken using the cryogenic-background LABCEDE facility at the Phillips Laboratory. Mixtures of CO, Ar, and N_2 at pressures of 2-40 millitorr were irradiated with a pulsed 4-5 keV electron beam, and the resulting time-resolved infrared CO spectra were obtained with a Michelson interferometer capable of 2 cm^{-1} resolution. The spectra were highly self-absorbed in the v=1-0 band, but not in the highly vibrationally and rotationally excited bands. The complex, overlapped, and partially self-absorbed spectra were analyzed using pattern recognition algorithms, and excellent agreement between data and fit was obtained. Vibrational basis sets (patterns) were obtained both from synthetic spectral models and from the XCC (Extended Cross- Correlation) method. A global fit using this combined model was performed, in which the time dependence of the known basis sets and the XCC patterns was determined. Applications of this method include remote sensing of environments in which the optical properties of the line of sight are poorly known, where spectroscopic basis sets are unavailable, or where spectra change with time or viewing angle, such as in the aurora or other highly structured atmospheric scenes.

The IR spectrum of ammonia is very complex, especially for the nonsymmetic ND_2H and NDH_2 isotopomers. Analysis of such a spectrum is enormously simplified when the raw mixed-isotopomer spectrum is separated by a model- and assignment-free method into spectra of separate isotopomers! By recording spectra

of equilibrated sample at several H/D ratios, the XCC scheme unzips the raw spectra into single isotopomer spectra. This work was done by Steve Coy and Jason Clevenger in collaboration with Dr. Linda Brown and Dr. Jack Margolis (Jet Propulsion Laboratory), and Dr. Michael Dulick (Kitt Peak National Observatory). Similar unzipping schemes are under discussion with Professor David Nesbitt (JILA) for H_2O and H_3O^+, but are better suited for FTIR than cw tunable laser spectroscopy.

d. Resonance Enhanced Multiphoton Ionization (REMPI) Apparatus.

A pulsed jet molecular beam apparatus with REMPI-TOF capabilities has been constructed by Chris Gittins (Ph.D. 2/95). Although so far this apparatus has been used primarily in NSF supported studies of Rydberg states of CaF, CaCl, and BaF, it was constructed and will be available for time-shared use in REMPI-TOF studies of triplet acetylene.

e. Ionization Energies of CaF and BaF.

Mass spectrometric data, recorded by Edmund Murad and James Gardner at the Air Force Phillips, and low principal quantum number Rydberg state data obtained by Jakubek, Harris, and Gittins at MIT, were combined to yield accurate ionization energies. This represents another transition between a university laboratory and an Air Force laboratory.

B. Publications (Since 1986) Resulting from AFOSR Support

The research of the Co-PI's is supported by AFOSR and DOE grants in the general area of the spectra of vibrationally highly excited polyatomic molecules. The distinction between these two funded projects is discussed in the original research proposals. We list below all of our publications relevant to the research described in the present project; AFOSR support is denoted by (+) and DOE support by (++).

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C. Ph.D. Theses (Since 1986) Resulting from AFOSR Support

The research of the Co-PI's is supported by AFOSR and DOE grants in the general area of the spectra of vibrationally highly excited polyatomic molecules. The distinction between these two funded projects is discussed in the original research proposals. We list below all of our Ph.D. Theses relevant to the research described in the present project; AFOSR support is denoted by (+) and DOE support by (++).

+	9/86	Vaccaro, Patrick H.	Spectroscopy and Kinetics of Highly Excited Formaldehyde
(+,++)	9/87	Cameron, Stewart M.	Photon Echo Studies of Quantum Diffractive Superposition State Scattering Kernels
++	7/88	Chen, Yongqin	Spectroscopic Studies of Highly Excited Acetylene
+	8/89	Green, Peter G.	Acetylene Near Dissociation: Novel Effects of External Fields
+	1/90	Halle, Scott D.	Spectroscopic Studies of Collision-Induced Energy Transfer and Intramolecular Dynamics of Formaldehyde
+,++	2/92	Lundberg, James K.	Double Resonance Studies of Electronically Excited Acetylene
+,++	6/92	Jonas, David M.	Spectroscopy of Vibrationally Hot Molecules: Hydrogen Cyanide and Acetylene

++	7/94	Adamson, George W.	The Spectroscopy of the Formyl Radical
(+)	9/94	Schmid, Günther M.	Dynamical Symmetry Breaking in Molecules and Molecular Aggregates.
+	1/95	Rajaram, Bhavani	Optical-Optical Double Resonance Study of the $3\ ^1A'$ State of HCP
(+)	2/95	Gittins, Christopher	Electronic Structure and Electronic-Vibrational Energy Exchange in Rydberg States of Calcium Monofluoride
++	5/96	Solina, Stephani	Molecular Dynamics in Acetylene: From Spectra to Polyads to Dynamics
(++)	5/96	Bloch, Jonathan	Extending Frequency Modulation Spectroscopy: Sensitive and Selective High Resolution Laser Absorption in the Visible and Ultraviolet